Polydiacetylene Thin Films for Photonic Applications

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The goal of this work is to access the role of fluid flow on the formation and properties of polydiacetylene thin films for photonic applications such as nonlinear waveguiding and all-optical switching. Researchers at MSFC have been investigating polydiacetylenes (PDA), as well as other organic and polymeric nonlinear optical (NLO) materials, for the past several years. As a result of this research, a simple, novel technique for the photo-deposition from solution of thin amorphous films (on the order of a micrometer) of a polydiacetylene (PDAMNA) derived from 2-methyl-4-nitroaniline has been developed (U.S. Patent No. 5,451,433). During the course of this process, radiative heating by UV light produces thermal gradients in the solution; also, variations in the chemical composition of the solution caused by photo-polymerization causes solutal gradients. These density gradients, under the influence of Earth's gravity, induce natural convection in the system. This convection affects heat and mass transport to and from the growing film, and thereby affects the microstructure, morphology, and properties of the film. Preliminary numerical simulations of the fluid flow indicate that convection is present in the system even under conditions often thought to be gravitationally stable.[1]

One area in which experimental results have established that convection plays a role is defect formation: films grown in 1-g contain small (submicron) solid particles embedded throughout. These particles can scatter light and thereby lower the optical quality of the films. The particles consist of precipitated polymer which forms in the bulk solution, and get transported by convection to the surface of the growing film where they become embedded. In some cases the particles may actually nucleate on the film surface itself. By varying the orientation of the growth chamber with respect to gravity to minimize convection, the concentration of particles in the films can be reduced but not eliminated (fig. 144). Last September an experiment (PTFG–CONCAP IV–03) was flown aboard Endeavor (STS–69) in which films were grown in the reduced convection environment of microgravity. While results varied among samples, the best space-

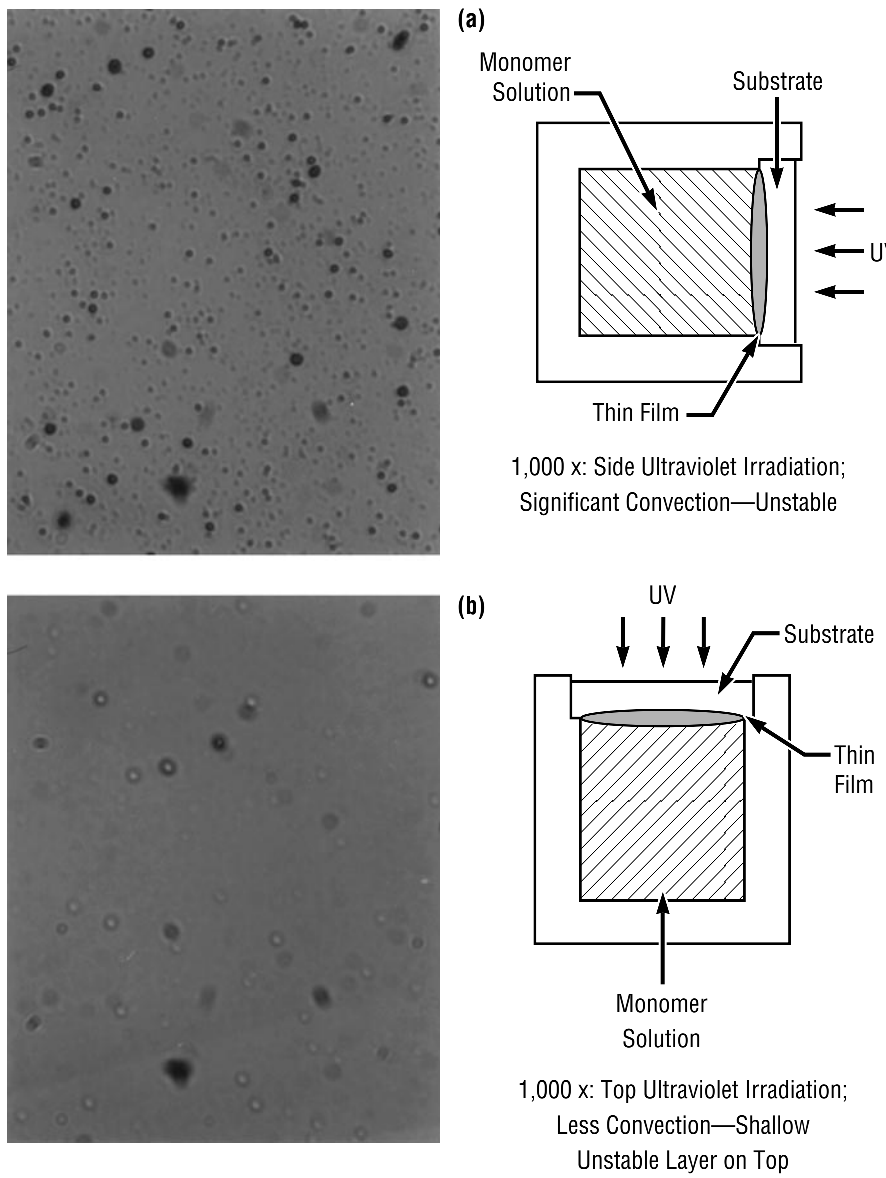

FIGURE 144.—PDAMNA films grown in two different orientations: a) films grown with the chamber horizontal; b) films grown with the chamber vertical.

grown films clearly exhibited fewer defects than the best ground-based films (fig. 145). This demonstrates that reducing convection can result in higher quality polydiacetylene films.

Not only can convection affect the transport of particles which are formed in the solution, it can also transport colloidal particles which are purposely introduced into the system to alter the optical properties. For example, small metal nanoparticles incorporated into a nonlinear host polymer can be used to enhance the nonlinearity and also reduce undesirable effects such as two-photon absorption, which causes loss. Researchers at MSFC have successfully prepared gold colloids in organic solvents, which, in turn, provides a means for getting the particles into polymer hosts.[2] PDAMNA films containing gold nanoparticles are readily obtained using photodepositon from such organic gold colloids. The resulting films, however, suffer from gradients in the metal concentration which most likely result from convection. In order to achieve the desired optical properties, uniform concentration of the metal colloid is neccessary. Processing in a diffusion-controlled environment could thus be quite beneficial.

Preliminary studies conducted at MSFC of the rate law for polydiacetylene film photodeposition indicate that the rate of film growth depends linearly on UV radiation intensity and, interestingly, on the square root of monomer concentration.[3] Also, it is known that the rate increases with higher temperature. Because convection affects the temperature and concentration profiles along the surface of the growing film, the rate of film growth will likewise be affected. Variations in the growth rate along the surface can lead to uneven film growth; this is manifested in the thickness and surface roughness of the films.

In addition to affecting the formation and/or distribution of bulk particles in polydiacetylene films photodeposited from solution, convection may also affect the molecular orientation. Recently, researchers discovered that these films exhibit partial alignment of the polymer chains normal to the substrate surface. This is important because ordered films are desired for many applications. Convection may be detrimental to obtaining well-ordered films. It has been observed that in 1-g films grown for short durations of time are more highly ordered than those grown for longer durations. This could be a result of convection; the turbulent and chaotic molecular motions that take place during convection could cause the polymer chains to become entangled and matted around each other as they grow longer. The use of moieties chemically incorporated into the polydiacetylene structure is being investigated to aid in inducing self-alignment of the polymer chains.[4] At Rice University, a student researcher is performing synthetic modifications to PDAMNA which appear to exhibit the desired behavior.

CONCAP IV-3 PTFG Cell 9

FIGURE 145.—PDAMNA films grown in space. The best space-grown films clearly exhibit fewer particles than the best ground-based films.

[1]Frazier, D.O; Hung, R.J.; Paley, M.S.; Long, Y.T.: *Journal of Crystal Growth,* in press, 1996.

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[3]Paley, M.S.; Armstrong, S.; Witherow, W.K.; Frazier, D.O.: Chemistry of Materials, 8(4), 912, 1996.

[4]McArdle, C.B.: Ed., Side Chain Liquid Crystal Polymers. Publication: Chapman and Hall, NY, 1989.

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University/Industry Involvement: Mark S. Paley, principal investigator, Universities Space Research Association (USRA); Optron Systems, Inc., Bedford, MA

Biographical Sketch: Donald O. Frazier is a senior scientist for physical chemistry at MSFC. Frazier earned his Ph.D at Rutgers University. He develops research programs which focus on microgravity processing for fundamental and applications sciences. He also serves as project scientist for ground-based and flight programs, and establishes educational outreach relevant to ongoing projects. In addition, he promotes technology transfer relevant to research programs.